

1-23-01

AFRL-SR-BL-TR-01-

REPORT DOCUMENTATION PAGE

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1. REPORT DATE (DD-MM-YYYY) 29-12-2000		2. REPORT TYPE Final Technical		3. DATES COVERED (From - To) 1 Jun 97 - 31 May 00	
4. TITLE AND SUBTITLE (AASERT97) Dynamics of Elementary Termolecular Reactions and Cluster Fragmentation				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-97-1-0387	
				5c. PROGRAM ELEMENT NUMBER	
				5d. PROJECT NUMBER	
6. AUTHOR(S) Dr. Robert E. Continetti				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
				8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UC San Diego Dept Chemistry & Biochemistry 9500 Gilman Drive La Jolla, CA 92093-0340 Dr. Robert E. Continetti E-Mail: rcontinetti@ucsd.edu				10. SPONSOR/MONITOR'S ACRONYM(S)	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph Street Room 732 Arlington, VA 22203-1977				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT AF DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This grant supported research and training associated with studies of the energetics and dynamics of transient species and termolecular reactions.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 9	19a. NAME OF RESPONSIBLE PERSON Dr. Robert E. Continetti
a. REPORT Unclass	b. ABSTRACT Unclass	c. THIS PAGE Unclass			19b. TELEPHONE NUMBER (include area code) 858-543-5559

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1-23-01

Dynamics of Elementary Termolecular Reactions and Cluster Fragmentation

Final Technical Report - AFOSR AASERT Grant #F49620-97-1-0387

6/1/97 - 5/31/00

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1. Objectives

The objectives of this AASERT award (F49620-97-1-0387) were to provide funds for research and training support of graduate and undergraduate students in conjunction with AFOSR funded projects on the Dynamics of Elementary Termolecular Reactions (F49620-96-1-0220) and the successor project on the Spectroscopy and Dynamics of Transient Energetic Species (F49620-000-10-010). The scientific goals of these projects focus on the characterization of exotic neutral species and processes of potential importance in the upper atmosphere and high-pressure reactive environments. The experimental effort makes use of negative-ion photodetachment to prepare transient neutral molecules and clusters as precursors to three-body dissociation reactions. The training aspect of the AASERT grant has been well-served by the development of a new state-of-the-art multiparticle detector to allow these experiments to be carried out.

2. Accomplishments/New Findings 6/1/97 - 5/31/00

In the period of this grant the first detailed coincidence studies of three-body dissociation processes of neutral molecules was achieved. This effort involved the construction of a state-of-the-art fast ion beam apparatus and a new multiparticle detector, a process which was initiated one year prior to the award of the AASERT grant. The AASERT grant supported one graduate student, A. Khai Luong, for the full three years and provided partial support of two additional graduate students, Todd Clements and Christopher Laperle, in the last year of the grant. In addition, two undergraduate students were supported, Jacqueline Kessler (currently a graduate student at the California Institute of Technology) and Raymond W. Liu (currently a medical student at the Johns Hopkins University). In this section, the three most important contributions (first-authorship) from the graduate AASERT fellows A. Khai Luong and Todd Clements are reviewed in some detail. The third AASERT fellow, Christopher Laperle, is just beginning his studies, so he did not author any papers during the AASERT fellowship. The undergraduate students primarily worked on ion source and ion beam development.

2a. Three-Body Dissociative Photodetachment of $O_3^-(D_2O)$

The three-body recombination reaction $O + O_2 + M \rightarrow O_3 + M$ is responsible for the formation of stable ground state O_3 in the atmosphere. Therefore this system is an important prototypical three-body system for our detailed dynamics studies. A. Khai Luong made the study of this system one of her first priorities, as reported in Publication 3 in section 4a. of this report.

These experiments first focused on photoelectron spectroscopy to provide information on the energetics of the system. From these studies, we determined that $O_3^-(D_2O)$ is bound by 0.75 eV relative to $O_3^- + D_2O$, and that the electronic structure of O_3^- is largely unperturbed by clustering with D_2O via a charge-dipole interaction. Since three-body dissociative photodetachment can only be observed by photodetachment to one of the low-lying dissociative electronic states of O_3 , this meant that an ultraviolet laser had to be used. In the present study, we used the 258 nm 3rd harmonic of a Ti:Sapphire laser. With

these 4.80 eV photons, the dissociative states of the complex could be prepared. The interesting three-body intracuster reaction, $\text{O}_3(\text{D}_2\text{O}) \rightarrow \text{OD} + \text{OD} + \text{D}_2\text{O}$, however, is only energetically accessible by 0.16 eV. Since dissociation of the lowest triplet and singlet excited states populated by photodetachment at 258 nm yield ground state $\text{O}(^3\text{P})$ which is expected to have a large barrier for hydrogen abstraction from water, it was not surprising that we observed no evidence for this reaction pathway.

In paper 6 of section 4.a, we reported the photoelectron-photofragment kinetic energy correlation spectrum for $\text{O}_3^-(\text{D}_2\text{O})$ at 258 nm. This spectrum illustrates the correlation between the translational energy release (E_T) between the fragments and the photoelectron kinetic energy (eKE). The E_T spectrum for $\text{O}_3^-(\text{D}_2\text{O})$ features a broad peak with a maximum at 0.45 eV. This is very similar to the dissociative photodetachment of free O_3^- , previously studied in this laboratory. The eKE spectrum has considerably less resolved structure than that of free O_3^- , which is perhaps not surprising given the larger number of degrees of freedom and the potentially much faster predissociation in the perturbed complex. The similarities with free O_3^- , however, indicate that energy partitioning in the three-body dissociative photodetachment of $\text{O}_3^-(\text{D}_2\text{O}) + h\nu \rightarrow \text{O} + \text{O}_2 + \text{D}_2\text{O} + e^-$ is little affected by the presence of the third body, D_2O .

The detailed dynamics of the three-body dissociation of the excited $\text{O}_3(\text{D}_2\text{O})$ complex can be studied by examining the angular correlations of the product recoil vectors. Since all the products are detected in coincidence, this was done in the present experiments and presented in the form of a new observable, the molecular frame-differential cross section (MF-DCS). The MF-DCS is generated by transforming the data from the laboratory frame to a molecular break-up frame such that for each event, the velocity vector of the O atom is chosen as the principal axis and the recoil velocities of the other two particles are then plotted in this center-of-mass reference frame. The mass-resolution in these experiments is currently limited -- O_2 can be fully resolved from O and D_2O , but they cannot be fully resolved from one another. Due to this limitation, the assumption is made in generation of the MF-DCS that the O atom is the fastest particle. The MF-DCS shows that the centroid of the O_2 distribution recoils backward relative to the O atom, while the centroid of the D_2O feature is actually observed to be slightly forward-scattered relative to the recoiling O atom. The striking result from the MF-DCS is that the product momenta are partitioned such that the heaviest fragment, O_2 , carries away most of the momentum, with the lighter O and D_2O fragments recoiling in the other direction in the CM.

To gain further insights into the three-body dissociation dynamics indicated by the MF-DCS, we carried out density functional theory (DFT) calculations of the structure of the parent $\text{O}_3^-(\text{D}_2\text{O})$ complex. Two local minima were found, an asymmetric C_s complex with D_2O hydrogen bonded to one end of O_3^- and a double-hydrogen-bonded C_{2v} complex. By using the MF-DCS in conjunction with these DFT calculations, the most likely geometry of the complex at the time of the molecular break-up was deduced. In the structure with C_s symmetry, the cluster only forms one hydrogen-oxygen interaction between the two monomers. The calculated C_s geometry indicates that the O-D bond in the water moiety and the O- O_2 bond nearest the intracuster interaction are both longer than their respective ground state bond lengths, consistent with an ion-dipole interaction between the two moieties. This breaking of the C_{2v} symmetry of O_3 in the cluster is expected to promote the antisymmetric stretch dissociation of the lengthened O- O_2 bond,

which has been shown to be the reaction coordinate for dissociation of the low-lying excited states of O_3 in previous studies. This initial structure can be consistent with the observed partitioning of momentum if the lengthened bond breaks, causing the recoiling O atom to interact nearly elastically with D_2O , but in the process transferring a significant fraction of its momentum to the D_2O . The heavier O_2 product then carries away most of the momentum as it recoils in the other direction. Dissociation of the C_{2v} symmetry complex would not be expected to lead to such a striking partitioning of momentum between the light and heavy fragments.

To summarize, these experiments on the DPD of $O_3^-(D_2O)$ provided insights into the energetics of the anion and the three-body dissociation dynamics of excited electronic states of the neutral complex. Photodetachment to the triplet states of O_3 in the complex leads to three-body dissociation, with no clear evidence observed for intracuster reaction or quenching of the excited states in the complex at the level of excitation used in this experiment. In addition, the MF-DCS shows that the partitioning of momentum among the products leads to most of the momentum carried away by O_2 , with O and D_2O recoiling in the opposite direction in the CM. Combining the observations made from the MF-DCS and theoretical calculations, it is possible to make structural inferences on the dissociating neutral complex and the precursor anion. The results are most consistent with an $O_3^-(D_2O)$ complex of C_s symmetry found by DFT calculations.

2.b. Three-Body Dissociation Dynamics of O_6^-

Since oxygen plays a central role in both ion and neutral chemistry in atmospheric, plasma and combustion environments, studies of the oxygen trimer anion, O_6^- , were carried out. These efforts are described in publications 1,2 and 5 cited in section 4.a. of this report. Building on earlier studies of the dimer anion O_4^- , experiments were conducted with the new photoelectron-multiple-photofragment spectrometer that allow a detailed insight into the three-body dissociation dynamics that ensues upon the dissociative photodetachment of O_6^- : $O_6^- + h\nu \rightarrow O_2 + O_2 + O_2 + e^-$. In this system, the photoelectron-photofragment correlation spectrum reveals several processes, and provides considerable insight into the dissociation dynamics of O_6^- . Four diagonal features are observed in the spectrum, similar to our previous studies of O_4^- , that correspond to direct three-body dissociative photodetachment of $O_6^- + h\nu \rightarrow O_2 + O_2 + O_2 + e^-$ on vibrationally adiabatic repulsive surfaces. The spacing of these features in internal energy corresponds to 0.19 eV, the vibrational spacing of O_2 . There are also two other features observed, one arising from the photodissociation $O_6^- + h\nu \rightarrow O_2(^1\Delta_g, v=0) + O_2(^2\Pi_g, v=0) + O_2(^3\Sigma_g^-)$. The analogous process was seen in O_4^- . A new process was observed in O_6^- : photodissociation to vibrationally excited O_2^- and the ground states of the two other O_2 products: $O_6^- + h\nu \rightarrow O_2(^2\Pi_g, v>3) + O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$. This process leads to resolved features in the photoelectron spectrum owing to rapid vibrational autodetachment of the $O_2(^2\Pi_g, v>3)$ products of this photodissociation. Thus, the addition of a third O_2 to O_4^- has a significant effect on photodissociation processes, but evidently much less influence on the photodetachment dynamics. This is not to say that there is no effect on the O_2 product state distribution, however. The dissociative photodetachment of O_6^- is observed to yield considerably higher vibrational excitation than in the case of O_4^- . This implies that the

nuclear and electronic structure of O_6^- is more complicated than simply an O_4^- core with a weakly bound O_2 , or alternatively a molecular anion in which the excess electron is fully delocalized over the three O_2 molecules.

2.c. Three Body Dissociative Photodetachment of $O^-(H_2O)_2$ and $OH^-(H_2O)_2$ and Deuterated Analogues

AASERT fellow Todd Clements focused his efforts on a study of the interaction of reactive species such as the O atom and the OH radical with solvating water molecules. The first manuscript reporting these studies has been submitted to the Journal of Chemical Physics (publication 1 in section 4.c.). The three-body dynamics of these systems are important in that they may yield insights into the structure and behavior of these reactive species in both condensed and high-pressure gas-phase environments, such as might be encountered in an expanding rocket exhaust. In the case of $O^-(D_2O)_2$, the photoelectron-photofragment correlation spectrum and the MF-DCS. In this system two product channels are accessible, $O + 2 D_2O + e^-$ and $OD + OD + D_2O$. Regrettably the current mass-resolution of the experiment prevents a clean resolution of these channels, although a significant difference in the energetics allows the former channel to be studied in isolation for low levels of product excitation. The MF-DCS in this system shows that all three products carry away comparable amounts of linear momentum, in striking contrast to the previously studied systems, O_6^- and $O_3^-(D_2O)$ discussed above. In the case of O_6^- , two of the O_2 products carry away equal momenta, imparting only a small amount to the third O_2 . In the case of $O_3^-(D_2O)$, the heavy product, O_2 , carries away most of the momentum. Calculations of the structure of the $O^-(D_2O)_2$ anion are underway to aid in the interpretation of these observations. We have also observed three-body dissociative photodetachment of the $OH^-(H_2O)_2$ cluster anion. In this system, only one product channel, $OH + 2 H_2O + e^-$, is accessible so mass resolution is not a critical issue. Once again it was found in this system that there is a roughly equal sharing of momenta between the three photofragments, consistent with a cluster anion with a range of starting geometries.

3. Personnel Associated with the Research Effort

As noted in the introduction to section 2, this AASERT grant has partially supported the research and training of three graduate students (A. Khai Luong, Todd Clements and Christopher Laperle) as well as two undergraduate students (Jacquelyn Kessler and Raymond W. Liu).

4. Publications

Over the course of this AASERT grant, a number of papers have appeared citing AASERT support, as detailed here.

4a. Published

1. K.A. Hanold, A.K. Luong and R.E. Continetti, "Complete Kinematic Measurement of Three-Body Reaction Dynamics: Dissociative Photodetachment of O_6^- at 532 nm.", *Journal of Chemical Physics*, **109**, 9215-9218 (1998).
2. K.A. Hanold, A.K. Luong, T. Clements and R.E. Continetti, "Photoelectron-Multiple-Photofragment-Coincidence Spectrometer.", *Review of Scientific Instruments* **70**, 2268-2276 (1999).
3. A.K. Luong, T.G. Clements and R.E. Continetti, "Three-body Dissociation Dynamics of Excited States of $O_3(D_2O)$.", *J. Phys. Chem. A* **103**, 10237-10243 (1999).
4. H.-J. Deyerl, A.K. Luong, T.G. Clements and R.E. Continetti, "Transition State Dynamics of the $OH + H_2O$ Hydrogen Exchange Reaction Studied by Dissociative Photodetachment of $H_3O_2^-$.", *Faraday Discussion* **115**, 147-160 (2000).
5. A.K. Luong, T.G. Clements and R.E. Continetti, "Three-body Dissociation Dynamics of Neutral Transient Species: Dissociative Photodetachment of O_6^- .", *ACS Symposium Series Vol. 770, Imaging in Chemical Dynamics*, eds. A.G. Suits and R.E. Continetti, ACS, Washington DC (2000), pp. 312-325.

4b. In Press

1. A.K. Luong, T.G. Clements, M.S. Resat and R.E. Continetti, "Energetics and Dissociative Photodetachment Dynamics of Superoxide-Water Clusters: $O_2^-(H_2O)_n$, $n = 1-6$ ", *J. Chem. Phys.* (in press).

4c. Submitted

1. T.G. Clements, A.K. Luong, H.-J. Deyerl and R.E. Continetti, "Dissociative Photodetachment Studies of $O^-(H_2O)_2$, $OH^-(H_2O)_2$ and the Deuterated Isotopomers: Energetics and Three Body Dissociation Dynamics.", *J. Chem. Phys.* (submitted Nov. 2000).

5. Interactions/Transitions

5.a. Meetings and Presentations

Over the course of this AASERT grant, the PI gave a number of invited talks at universities, laboratories and international conferences as detailed in the progress reports of the parent AFOSR grant. Of more importance for evaluation of the AASERT grant however, are the presentations made by the AASERT fellows, which are detailed here.

1. K.A. Hanold, A.K. Luong and R.E. Continetti, "Three-Body Dissociation Dynamics: Photodissociation and Dissociative Photodetachment of O_6^- at 532 nm.", Gordon Conference on Molecular and Ionic Clusters, Ventura, CA, January 1998. (Poster)
2. A.K. Luong, T. Clements, K.A. Hanold and R.E. Continetti, "Photoelectron-Photofragment Coincidence Studies of Three-Body Dissociation Dynamics.", AFOSR Molecular Dynamics Contractor's Meeting, Monterey, CA May 18, 1998. (Poster)
3. A.K. Luong, T.G. Clements, R.E. Continetti, "Three-body Decay Dynamics of Transient Molecules.", 27th Conference on the Dynamics of Molecular Collisions, July 18-23, 1999. (Poster)
4. T.G. Clements, A.K. Luong, and R.E. Continetti, "Monte Carlo Modeling of Three Body Systems: Mechanisms of Dissociation.", Gordon Conference on Photoions, Photoionization, and Photodetachment, July 18-23, 1999. (Poster)
5. T.G. Clements, A.K. Luong, H.-J. Deyerl and R.E. Continetti, "Energetics and Three Body Dissociation Dynamics of $O^-(H_2O)_2$, $OH^-(H_2O)_2$ and Their Deuterated Isotopomers.", Conference on Molecular and Ionic Clusters, Toulouse, France, April 16-20, 2000. (Poster)
6. A. K. Luong, T. G. Clements and R. E. Continetti, "Dissociation Dynamics of Small Superoxide Hydrates.", Gordon Conference on Atomic and Molecular Interactions, New Hampshire, July 2000. (Poster)
7. A.K. Luong, T.G. Clements and R.E. Continetti, "Dissociation Dynamics of Small Water Cluster Anions.", Symposium on New Frontiers in Reaction Dynamics, Pacificchem 2000, Honolulu, HI Dec. 14-19, 2000. (Contributed Talk)

5.b. Consultative/Advisory Functions

The P.I. has maintained contact with the ion chemistry group at AFRL Hanscom. This has included consultations with Dr. Rainer Dressler at the Phillips Lab, Hanscom AFB (PL/GPOS) concerning isomeric structures of cluster anions throughout the past year. In addition, Dr. Skip Williams and Dr. Al Viggiano visited UC San Diego at separate times during the period of this grant, and further discussions with them have motivated our

interest in carrying out studies of three-body electron-ion recombination processes that constitute part of a DURIP proposal currently under consideration at the AFOSR.

The P.I. has also been in contact with Drs. Jay Levine and Ingrid Wysong at AFRL Edwards. These discussions have focused on the potential to determine product state distributions in reactions of O atoms and water molecules. We are currently carrying out studies of $O + H_2O$ for DOE, but to make a connection to high pressure phenomena, we are studying the $O(HD_2O)_2$ system as discussed in the results section above. To make real contributions to these problems, however, we will need to use a higher photon energy to access the $O(^1D)$ excited state.

5.c. Transitions

The P.I. has continued a collaboration with Dr. Carl Hayden at the Combustion Research Facility at Sandia National Laboratories, Livermore. This collaboration has resulted in the construction of the photoionization version of the photoelectron-photofragment spectrometers pioneered in the P.I.'s laboratory. The first published paper from this work has now appeared. In the next year, efforts will be made to implement delay-line detector technology, as pioneered in the quad-crossed-delay-line detector used in the studies of three-body dissociation processes reported here.

6. New Discoveries, Inventions or Patent Disclosures

Outside of the results reported in the accomplishments/new findings section above, there is nothing further to report here.

7. Honors/Awards

The P.I. received an Alfred P. Sloan Research Fellowship in 1997. This \$35,000 fellowship was given in recognition of the research accomplishments and future potential of the P.I.

The primary AASERT fellow, A. Khai Luong, received the UCSD Chemistry and Biochemistry Teddy G. Traylor award for excellence in research, including a \$1000 cash prize, in 1999.